Journal of Photochemistry and Photobiology A: Chemistry 356 (2018) 451–456

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Hydrogen generation by photocatalytic reforming of potential biofuels: Polyols, cyclic alcohols, and saccharides

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ARTICLE INFO

Article history:
Received 8 September 2017
Received in revised form 9 January 2018
Accepted 22 January 2018
Available online 31 January 2018

Keywords:
Hydrogen
Photocatalysis
Water splitting
Biofuels
Polyol
Sugar

ABSTRACT

We have studied hydrogen gas production using photocatalysis from C2-C5 carbon chain polyols, cyclic alcohols and mono and di-saccharides using palladium nanoparticles supported on a TiO_2 catalyst. For many of the polyols the hydrogen evolution rate is found to be dictated by the number of hydroxyl groups and available α-hydrogens in the structure. However the rule only applies to polyols and cyclic alcohols, while the sugar activity is limited by the bulky structure of those molecules. There was also evidence of ring opening in photocatalytic reforming of cyclic alcohols that involved dehydrogenation and decarbonylation of α C—C bond.

1. Introduction

Our reliance on fossil fuels as our primary source of energy has come under increasing scrutiny in recent years; mainly due to the effect of combustion products on our climate. Currently 86% of global energy utilisation and 75% of CO_2 emissions originate from fossil fuels [1]. Combustion of fossil fuels releases CO_2 into the atmosphere and is known to be one of the main contributors to global warming. There has long been an interest in the production and the safe storage of hydrogen as a fuel. One advantage of using hydrogen as a fuel source is that when it comes into contact with oxygen the energy is released cleanly, with the only by-product being water. Hydrogen production has already been approached by a variety of different methods, such as the reforming of steam from industrial processes [2], but perhaps the most exciting means of producing this fuel is through the splitting of water molecules into hydrogen and oxygen gases with three very simple components – water, natural light and a carefully selected catalyst. Hydrogen production from splitting water is an area of great research interest as it could provide an alternative to fossil fuels. However, pure water splitting is difficult but it has been found that using a sacrificial agent can increase the hydrogen yield dramatically by scavenging holes and thus extracting the oxygen from the system [3].

A main principle for a semiconductor to catalyse hydrogen production from photocatalytic water splitting is the hydrogen reduction potential should be above the energy required for water reduction [4]. TiO_2 is a popular choice of photocatalyst mainly due to its stability and narrow band gap of 3.2 eV that allows photon absorption in the UV region [5]. Modification of TiO_2 with anion or cation dopants is claimed to promote electron excitation in the visible light region, although much of this work is hindered by fast electron hole recombination [6–9]. For the TiO_2 to be able to catalyse the water splitting reaction, it requires metal nanoparticles at the surface to improve the rate of hydrogen production [10–12]. The role of the metal in improving catalytic activity has been widely investigated. A Schottky barrier is created between TiO_2 and metal which allows electrons generated in the conduction band of TiO_2 to be transferred to the metal surface. This prolongs electron and hole lifetimes. The metal also plays a role as an active site for water reduction. Pd [13], Pt [14,15], Ag [16], Au [17], Cu [18] have been reported to be active metals for water splitting when used in conjunction with a semiconductor and a hole scavenger. Studies reported by Li et al. on Au encapsulated with TiO_2,

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https://doi.org/10.1016/j.jphotochem.2018.01.031

highlighted that the Au role is to promote hydrogen association to leave metal surface by the reduction of protons on the TiO_2 surface [19]. Studies on various metal/TiO_2 systems shows that it is important for the metal to be in its reduced state for hydrogen to evolve [20].

Photocatalytic hydrogen production using bio-oxygenates is a potential alternative energy resource for the increasing energy demand. It is possible that the reaction could be driven solely by solar radiation making it a greener process with less CO_2 emissions compared to burning fossil fuels. Bio-oxygenates have been used in photocatalysis as sacrificial agents for water splitting. We suggested in previous works that the alcohol is not only acts as a sacrificial agent but is also contributing to the hydrogen gas formation [21]. The hydrogen atom in the alpha position of carbon hydroxyl in bio-oxygenates will dehydrogenate on the Pd surface and leaves as H_2 gas [22]. Studies by Fujita et al. using D_2O and glycerol showed that glycerol provides a main source of hydrogen with the presence of water shows positive effects in improving hydrogen yield [23]. Scavenging efficiency was found to be better in polyols with more OH groups [24]. Detail studies by Fu et al. suggested the OH groups produced a strong chemical adsorption between polyols and the Pd/TiO_2 catalyst surface [25,26]. Sugars are also considered renewable resources of energy which contain a high number of OH groups. Kondarides et al. tested a range of alcohols and sugars including glucose and proposed that the stoichiometry of the reaction can be predicted using the following reaction [27].

$$C_3H_{8-x}(OH)_x + (6-x)H_2O \rightarrow (10-x)H_2 + 3CO_2$$

We aim to obtain clear understanding on the mechanism of hydrogen production from bio-oxygenates and to examine potential bio-oxygenates that are active for hydrogen generation. Our previous work has determined the rule of activity for molecule in which the hydrogen atom alpha to hydroxyl group will be evolved as H_2 gas in photocatalytic reforming of oxygenates [22]. In this study we have investigated photocatalytic reforming of C2-C5 carbon chain polyols, cyclic alcohols and mono and di-saccharides in order to understand the effect of hydroxyl group orientation on the ability to produce hydrogen. Establishing the differences in activity of alcohols will aid understanding of the general mechanism of photocatalytic reforming reactions.

2. Materials and methods

Palladium nanoparticles were deposited on TiO_2 at 0.5% weight loading via the incipient wetness impregnation method. $PdCl_2$ solution was added dropwise onto TiO_2 support, followed by drying and calcination at 500 °C. The photocatalytic reaction was carried out in a 200 ml three necked flask made of Pyrex glass filled with 100 ml of deionised water and 0.2 g of catalyst and alcohol. The alcohols tested were methanol, ethylene glycol, glycerol, erythritol and xylitol. We also investigated the cyclic alcohols, cyclohexanol, 1,2, 1,3 and 1,4-cyclohexanediol including sugars molecule, glucose, sucrose and fructose. All the alcohols were obtained from Sigma Aldrich at ~99% purity. The amount of alcohols used were fixed at 0.0024 mol. The catalyst suspension and alcohol-water mixture was stirred with a magnetic stirrer and illuminated with a 400 W Xe arc lamp (Oriel model 66084) from the side of the flask. 0.2 ml gas sample was extracted from the reaction vessel by syringe and analysed using a Perkin Elmer Clarus 480 gas chromatograph with a thermal conductivity detector. Liquid product was separated from the catalyst after 3 h of reaction and analysed using liquid chromatography mass spectroscopy.

3. Results

3.1. Characterisation of the catalysts

Fig. 1 shows the XRD diffractogram of 0.5% Pd/TiO_2 catalyst after air calcination at 500 °C. XRD was used mainly to confirm the TiO_2 P25 crystalline structure which predominantly consists of anatase and rutile crystalline phases. However due to metal weight loading of Pd is only 0.5%, the peak corresponded to Pd was not detected in the XRD. The 0.5% Pd/TiO_2 was also subjected to XPS analysis as shown in Fig. 2. The Ti 2p and Pd 3d peak positions were calibrated using C 1 s signal at 284.8 eV [28–30]. The Ti 2p peak is sharp and intense, appeared at 459 eV indicates the catalyst consists of Ti^{4+} surface species only. We also observed the Pd 3d peak appeared at ~ 336.5 which corresponds to oxidised PdO [31,32]. The intensity of the Pd 3d peak is significantly lower than the Ti 2p due to the low loading of Pd on the catalyst.

3.1.1. Hydrogen from polyols

The volume of hydrogen gas produced from photocatalytic reforming reaction of methanol and C2-C5 polyols; ethylene glycol, glycerol, erythritol and xylitol were measured and the plot of hydrogen volume produced against reaction time is shown in Fig. 3a. These molecules were chosen due to the presence of a hydroxyl group for each atom carbon in the structure. Hydrogen production for methanol and the polyols increased linearly which indicates that there is a steady rate of reaction with negligible induction time. The volume of hydrogen production for the polyols increased with the number of hydroxyl groups from methanol to xylitol. 8 ml of hydrogen was produced from methanol and 23 ml of hydrogen from xylitol. The polyols were used in these reactions at the same molar concentration and therefore the additional number of hydroxyl groups in the structure evidently leads to a higher reactivity. Further analysis of the gas products was carried out after 3 h of reaction to determine the presence of CO_2 and any aliphatic gases compounds. CO_2 and H_2 were observed as the only product in the gas phase. Analysis of the liquid products showed no traces of products in solution apart from the reactant used in the reactions.

$$CH_3OH + 3H_2O \rightarrow 3H_2 + CO_2 \quad (1)$$

Fig. 3b shows the CO_2 production after 3 h of photocatalytic reaction. The CO_2 production from methanol to ethylene glycol increased by a factor of two, while glycerol shows a significant enhancement to give 4.3 ml in 3 h of reaction. However for C4 and C5 polyols, the volume of CO_2 is fairly similar over 3 h of reaction. The proposed overall reaction scheme for methanol reforming is shown in Eq. (1). The yield of hydrogen and carbon dioxide were

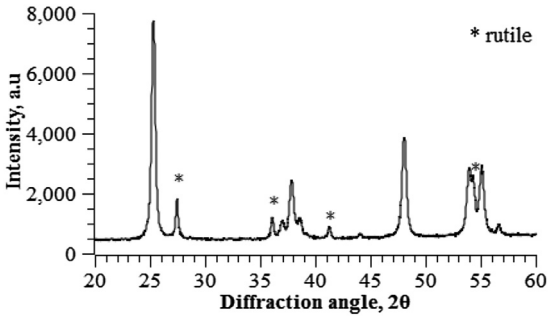

Fig. 1. X-ray diffractogram of 0.5% Pd/TiO_2 catalyst following calcination at 500 °C.

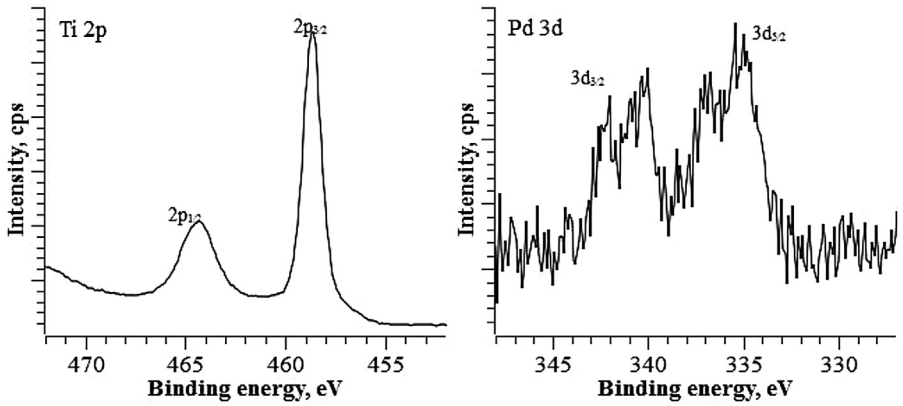

Fig. 2. Ti 2p and Pd 3d XPS analysis spectra of 0.5% Pd/TiO_2 catalyst.

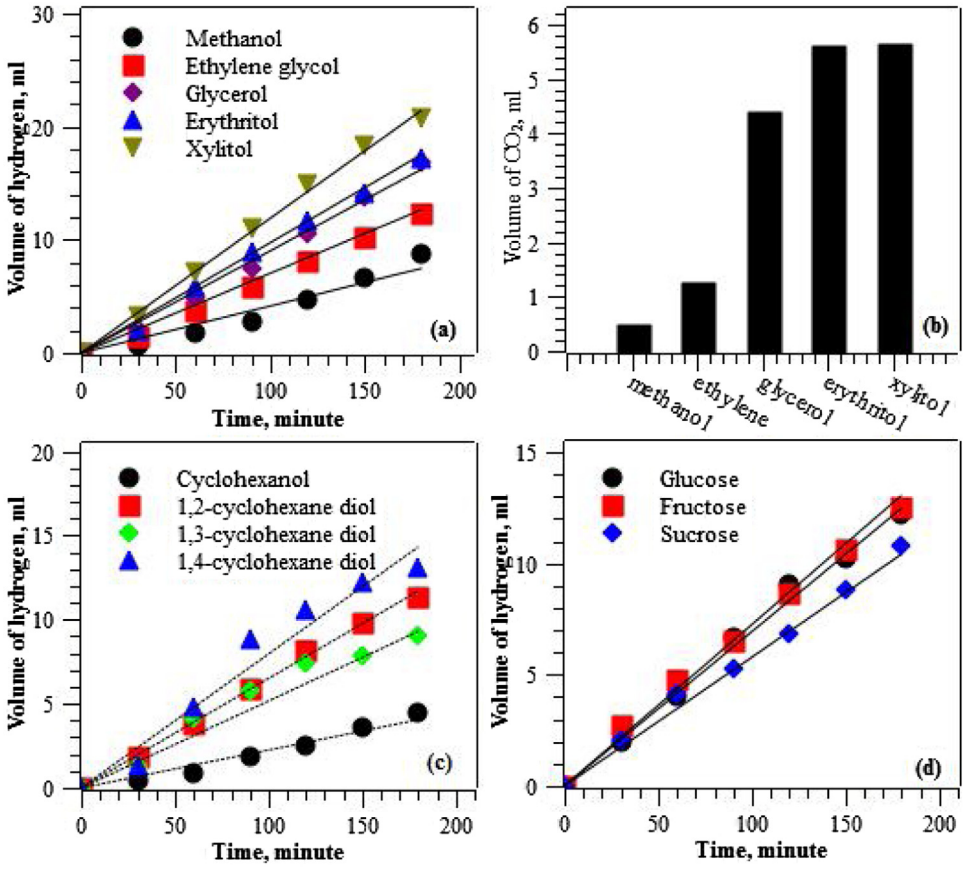

Fig. 3. Photocatalytic reforming of (a) methanol and C2-C5 carbon chain polyols on 0.5% Pd TiO_2 catalyst. (b) CO_2 gas production from C2-C5 carbon chain polyols on 0.5% Pd TiO_2 catalyst after 3 h. (c) Hydrogen plot from photocatalytic reforming of cyclic alcohol cyclohexanol and cyclohexanediols 1,2-cyclohexanediol, 1,3-cyclohexanediol and 1,4-cyclohexanediol. (d) Hydrogen production from photocatalytic reforming of sugar compounds, glucose, fructose and sucrose.

monitored over time to establish whether the reaction followed the stoichiometry. After 3 h of reaction, 9.0 ml of H_2 has been evolved but only 0.5 ml of CO_2 was detected. The H_2:CO_2 ratio here is higher than the expected 3:1 ratio. High H_2:CO_2 ratios have been reported and it was suggested that it was due to incomplete oxidation of CO_2 with CO being detected [33]. However, no CO was detected in this study. The high H_2:CO_2 ratio is due to dissolution of CO_2 in the reaction solution. This was confirmed by increasing the temperature of liquid solution to 60 °C for 30 mins at the end of reaction, and then the volume of CO_2 increases to reach 4 ml.

3.1.2. Hydrogen from cyclic alcohol and mono and di-saccharides

Hydrogen generation from cyclic alcohols and sugar compounds (mono and di-saccharides) were also investigated, and all of the molecules used were capable of photocatalytic hydrogen evolution. Using cyclohexanol, 4 ml of hydrogen was produced, while all three cyclohexane diols are active for hydrogen production with 1,4-cyclohexanediol producing the most hydrogen at ~13 ml in 3 h (Fig. 3c). 1,3-cyclohexanediol produces the least at 9 ml in 3 h. The gas phase products produced were given in Table 1. Only H_2 and CO_2 were identified for the reaction using 1,4-

Table 1
Product obtained from photocatalytic reaction of cyclohexane diol after 3 h of reaction.

Cyclic alcohol	Liquid analysis product	Gas product
Cyclohexanol,	Cyclohexanone,	H_2, CO_2
1,2-cyclohexanediol,	2-hydroxycyclohexanone,	H_2, CO_2, C_4H_{10}
1,3-cyclohexanediol,	3-hydroxycyclohexanone,	H_2, CO_2, C_3H_8
1,4-cyclohexanediol,	4-hydroxycyclohexanone,	H_2, CO_2

cyclohexanediol, whereas a mixture of H_2, CO_2 and *n*-butane was present in the gaseous product of 1,2-cyclohexanediol and H_2, CO_2 and *n*-propane evolved from 1,3-cyclohexane diol. The presence of *n*-butane and *n*-propane indicate ring-opening reactions occur for these molecules. Note that the volume of CO_2 detected for cyclic alcohol is significantly lower that the chain alcohols, with less than 0.15 ml in 3 h for all the cyclic alcohols measured.

We also carried out analysis of liquid products for cyclohexanols using GCMS, and the results were given in Table 1. Cyclohexanol photoreforming produced cyclohexanone. For all cyclohexanediols used the liquid product obtained is the result of an oxidation reaction of one hydroxyl group. 2-hydroxycyclohexanone was detected from 1,2-cyclohexanediol, 3-hydroxycyclohexanone was detected from 1,3-cyclohexanediol and hydroxycyclohexanone from 1,4-cyclohexanediol.

Photocatalytic reforming was further investigated using various sugars, and the results for glucose, fructose and sucrose are shown in Fig. 3d. The volume of hydrogen produced was fairly similar at around 10–12 ml after three hours. The number of hydroxyl groups in the sugars was varied but the activity was found to be similar. This is surprisingly low in comparison to the polyols. Xylitol, a 5-carbon polyol with 5 hydroxyl groups produces 20 ml of hydrogen within three hours of reaction, whereas glucose, a 6-carbon sugar with also 5 hydroxyl groups only produces 12 ml.

4. Discussion

Production of hydrogen gas from reforming reaction using solar energy is important, particularly to reduce the cost of energy use to drive the process. The concept of photoreforming implies the hydrogen generated from photocatalytic reaction is not solely comes from water splitting but significant hydrogen is contributed from available hydrogen atoms in the alcohol structure. The rate of hydrogen production increased when longer chain polyols was used in the reaction. Analysis of the by-products from polyols obtained after reaction showed only CO_2 and H_2 were detected suggesting the molecules underwent complete dehydrogenation and decarbonylation. In order to understand the mechanism of hydrogen production, the reactivity pattern of alcohol on pure TiO_2 and Pd surfaces were used to gain insights into the catalytic processes. Although most of the decomposition studies were carried out on the Pd model single crystal surfaces in UHV conditions [34–38], we have shown that methanol, ethanol and propanol photocatalytic reaction products mimic the decomposition pattern on the well-defined Pd metal surfaces [21,39]. Studies carried out by Griffin et al. on the decomposition of ethylene glycol on Pd showed similar characteristics to methanol decomposition [40]. Ethylene glycol was shown to adsorb on a Pd surface via its oxygen atom followed by elimination of the α-hydroxyl hydrogen resulting the ethylene dioxide [40]. This subsequently underwent C—C bond scission and dehydrogenation, producing hydrogen and adsorbed CO. Since the only products detected from photoreforming of ethylene glycol were H_2 and CO_2 and no significant induction period was observed we can therefore suggest that ethylene glycol followed similar mechanistic steps as methanol. Li et al. suggested that glycerol follows multiple oxidation steps with photogenerated hydroxyl radicals during reaction [41]. Gluconic acid, glucaric acid and arabitol [42] were reported as intermediates from photocatalytic reforming of glucose before the intermediates were decomposed further to give H_2 and CO_2. For every oxidation step, 1 atom carbon is removed from glucose to form formic acid [42]. The oxidation continues until the remaining intermediates decomposed into CO_2. Our previous studies on glycerol suggested the mechanism involved complete dehydrogenation and decarbonylation of glycerol on the Pd surface to give H_2 and adsorbed CO [22,43]. The CO was oxidised by photogenerated electrophilic oxygen species to CO_2. The cycle continues with water reduction that refills the oxygen vacancy and generating hydrogen gas.

For the rest of the polyols used in this study, the volume of hydrogen increased linearly with the number of hydroxyl group and the photoreforming reaction of polyols with water can therefore be summarised as below:

$$C_2H_4(OH)_2 + 2H_2O \rightarrow 5H_2 + 2CO_2 \quad (2)$$

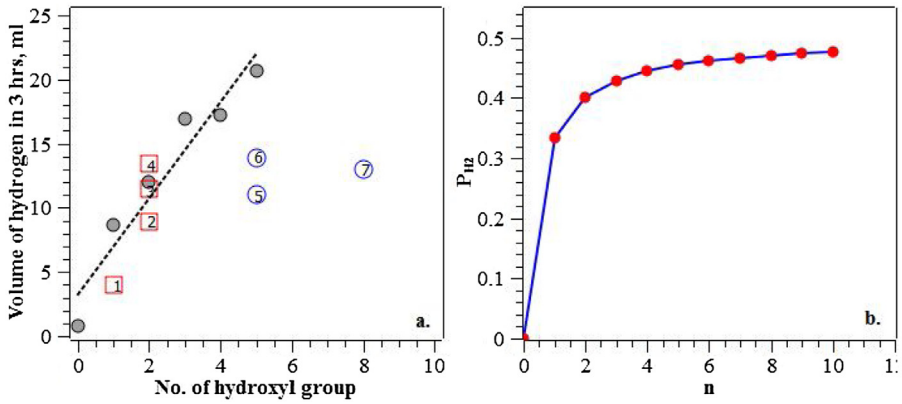

Fig. 4. A comparison of the rates of hydrogen evolution from the photoreforming reactions over the number of hydroxyl group in the structure. ● is represent data from CO, methanol and C2-C5 polyols; □ is for respective cyclic alcohols (1. cyclohexanol; 2. 1, 3-cyclohexanediol; 3. 1,4-cyclohexanediol; 4. 1,2-cyclohexanediol) and ○ is for sugars (5. fructose; 6. glucose and 7. sucrose). b. The proportion of total hydrogen evolved which derives from water itself, rather than from the alcohol.

$$C_3H_5(OH)_3 + 3H_2O \rightarrow 7H_2 + 3CO_2 \quad (3)$$

$$C_4H_6(OH)_4 + 4H_2O \rightarrow 9H_2 + 4CO_2 \quad (4)$$

$$C_5H_7(OH)_5 + 5H_2O \rightarrow 11H_2 + 5CO_2 \quad (5)$$

The graph illustrating the relationship between the numbers of hydroxyl groups in the structure with the volume of hydrogen produced after three hours of reaction is shown in Fig. 4a. A linear relationship was observed. It is also important to note that not only the hydroxyl group is involved in the hydrogen production, but all of the hydrogen in the structure is involved in photoreforming reaction as a result of oxidative decarbonylation. The number of moles of hydrogen, N_{H2} produced is simply related to the number of carbons (and OH groups) in the molecule in the following way –

$$N_{H2} = (2n + 1) \quad (6)$$

where n is the number of carbon atoms in the structure. The reaction basically involves oxidation of the C—O bond by water in 1:1 stoichiometry, combined with loss of the other H atoms at H_2. It is interesting to highlight the proportion of hydrogen that comes from water, P_{H2} for each of the polyols studied in the photoreforming process which is given by the following equation.

$$P_{H2} = n/(2n + 1) \quad (7)$$

Table 2 gives the molar fraction of hydrogen derived from the overall reaction and that from water splitting. The amount of hydrogen from water when methanol is used is ~ 33% and the ratio increases with the increase in polyol chain length, asymptotically approaching 50% as the chain length increases, as shown in Fig. 4b.

In an attempt to see if sugars and cyclic alcohols follows similar trend as polyols, we added the H_2 yield from sugars and cyclic alcohols into Fig. 4a. The figure reveals that cyclohexanol, with one hydroxyl group produced significantly less hydrogen than methanol. Analysis of the liquid solution filtrate showed ~ 17% of cyclohexanol conversion with cyclohexanone was the only product, meanwhile analysis of gas product showed a trace of CO_2 (and H_2 formation). Hydrogen generation may be the result of by-product of cyclohexanol oxidation to cyclohexanone. The presence of a trace of CO_2 (0.15 ml in 3 h) may also suggest further oxidation of cyclohexanone to CO_2. This process may be the rate determining step and therefore infers a slower rate of hydrogen generation. Looking at the rate of hydrogen production from cyclohexanediol, there is a significant improvement in comparison to cyclohexanol, suggesting the rules depicting the relationship between the number of hydroxyl group in the alcohol structures with the hydrogen rate may still applicable for cyclic polyols. The presence of additional hydroxyl groups in the cyclohexanediol structure accelerates hydrogen generation. Formation of alkanes as a result of decarbonylation of two C—O groups provides evidence of ring opening during the photoreforming process in these cases.

We might expect sugars to produce high rates of hydrogen evolution, since they have large numbers of hydroxy-functionalised C groups. However, the volume of hydrogen produced from mono and di-saccharides; glucose, sucrose and fructose were lower in comparison to polyols. It has been suggested that the rate of reaction is dictated by the molecular mass of sugar, due to slow diffusion through the reaction solution [44]. We compare glucose and fructose to xylitol which have similar molecular weights. Xylitol however, produces more hydrogen so the limitation may not only dictated by molecular weight but it may be that the ring structure of sugar adds some stability during for photoreforming reaction. The bulkier structures of sugar in comparison to the linear polyols may also result in less accessibility to active sites on the catalysts.

Table 2
The estimated fraction of hydrogen from water for each polyol.

Alcohol	Molar fraction	% hydrogen derived from water
Methanol	1/3	33
Ethylene glycol	2/5	40
Glycerol	3/7	42.8
Erythritol	4/9	44.4
Xylitol	5/11	45.5

5. Conclusion

This work has focussed on using different bio-oxygeneate sacrificial agents for hydrogen production and on understanding the mechanism of the reaction. A model predicting hydrogen production from polyols with varying OH groups was proposed. The sacrificial agents chosen followed the previous rules suggested by our group in which the availability of hydrogen in the structure influences the rate of hydrogen generation. Polyols and cyclic alcohols were found to fit the model, exhibiting a direct relationship between the number of OH groups and the number of moles of hydrogen produced.

Acknowledgement

Authors would like to acknowledge ESPRC for research funding for J. Kennedy, and UK Catalysis Hub for H. Bahruji and M Bowker. UK Catalysis Hub is kindly thanked for resources and support provided via our membership of the UK Catalysis Hub Consortium and funded by EPSRC (grants EP/K014706/1, EP/K014668/1, EP/K014854/1EP/K014714/1 and EP/M013219/1). E. Bouleghlimat was supported by the European Commission under FP7 project 309846, “Photocatalytic Materials for the Destruction of Recalcitrant Organic Industrial Waste (PCATDES)”.

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